



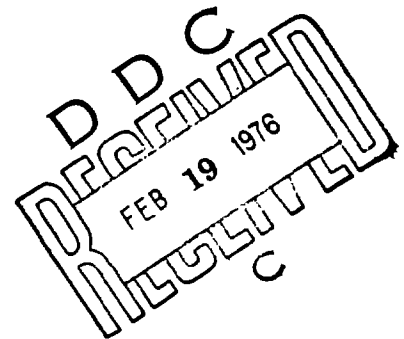
DEEP OCEAN HYDRAZINE DECOMPOSITION TESTING

by

R. T. Hoffman

Ocean Technology Department

January 1976



REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

Approved for public release; distribution unlimited.

ADA020808



NAVAL UNDERSEA CENTER, SAN DIEGO, CA. 92132

AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

R. B. GILCHRIST, CAPT, USN

Commander

HOWARD L. BLOOD, PhD

Technical Director

ADMINISTRATIVE INFORMATION

This report covers work performed to determine the decomposition efficiency of hydrazine at ocean depths of 20,000 feet.

The work reported herein was performed between July 1971 and September 1974, at the Hawaii Laboratory of the Naval Undersea Center (NUC). The work was sponsored by the Naval Material Command (NAVMAT 034), Deep Ocean Technology (DOT) program, with the Naval Sea Systems Command (SEA 03C, Project Number F33-313) acting as principal development activity.

This report was reviewed for technical adequacy and accuracy by K. W. Tate, Civil Engineering Laboratory, and T. W. Hughes, Naval Undersea Center.

Released by
J. D. Hightower, Head
Ocean Systems Division

ACCESSION for	
NTIS	Watts Section <input checked="" type="checkbox"/>
BEC	Duff Section <input type="checkbox"/>
UNCLASSIFIED	<input type="checkbox"/>
JUSTIFICATION.....	
BY.....	
DISTRIBUTION/AVAILABILITY NOTES	
Dist.	Avail. Sec/yr or other
A	

Authorized by
H. R. Talkington, Head
Ocean Technology Department

Mention of a commercial company or product does not constitute an endorsement by the Naval Undersea Center. Use for publicity or advertising purposes of information from this publication concerning proprietary products or the use of such products is not authorized.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NUC TP 495	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DEEP OCEAN HYDRAZINE DECOMPOSITION TESTING		5. TYPE OF REPORT & PERIOD COVERED Final Report, Jul. 71 to Sept. 74
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) R. T. Hoffman		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Undersea Center P. O. Box 997, Kailua, Hawaii 96734		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Material Command Washington, D. C. 20360		12. REPORT DATE January 1976
		13. NUMBER OF PAGES 34
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) hydrazine, gas generator, deep ocean gas source		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A hydrazine-fueled gas generator was built, instrumented, and tested <i>in situ</i> to obtain decomposition efficiency data. This test unit was completely self-contained and could be lowered to 20,000 feet by means of an available nylon line. Data obtained at 1060 feet verify laboratory results taken by the Naval Weapons Center, China Lake. A test unit failure at 17,700 feet prompted reconsideration of the physical properties of hydrazine. This evaluation culminated in laboratory testing which demonstrated that propellant-grade hydrazine will freeze at temperatures and pressures found in the ocean depths below approximately 9500 feet.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SUMMARY

Objective

The objective of this project was to determine the decomposition efficiency of hydrazine at ocean depths of 20,000 feet.

Approach

It was determined that the most cost effective approach was to design a hydrazine-fueled gas generator, instrument it, and test it *in situ* to obtain decomposition efficiency data. To this end a self-contained unit was built which could be lowered to 20,000 feet by means of an available nylon line.

Results

Decomposition efficiency data obtained at 1060 feet verify laboratory measurements made by the Naval Weapons Center (NWC), China Lake.

A test unit failure at 17,700 feet prompted reconsideration of the physical properties of hydrazine. This evaluation culminated in laboratory testing which demonstrated that propellant-grade hydrazine will freeze at temperatures and pressures found in the ocean at depths below approximately 9500 feet.

Conclusion

Neat or propellant-grade hydrazine cannot be used at ocean depths below approximately 9500 feet without a means of preventing freezing.

ACKNOWLEDGMENTS

The author wishes to extend his appreciation to Lcdr Savage, Commanding Officer, USS Reclaimer; Lcdr Fladd, Commanding Officer, USS Beaufort; and Roger Buecher, Naval Undersea Center, Code 6532, for their substantial efforts during the deep water testing at sea.

A special note of thanks is also due Herbert Mummery, Naval Undersea Center, Code 6534, for his skill and persistence in solving a myriad of small and large problems throughout the program.

CONTENTS

Summary	iii
Acknowledgments	iv
Introduction	1
Background	2
Approach and Ocean Hardware Development	2
Gas Generation System	3
Instrumentation System	6
Test Program	8
Test at 1000 Feet	8
Test at 3000 Feet	9
Test at 6000 Feet	10
Deep Ocean Tests	10
Discussion of Test Results	12
Laboratory Tests	15
Test Apparatus	15
Test Results	17
Discussion	18
Conclusion	19
Recommendations	19
Appendixes	
A. System Operation and Data Reduction	21
B. Theoretical Fusion Line for Hydrazine	24
Bibliography	26
Initial Distribution	27

INTRODUCTION

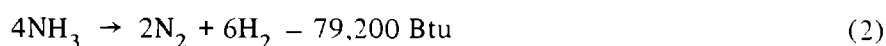
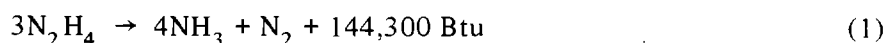
As submersibles attain greater and greater operating depths, the need arises for auxiliary recovery systems to assist in lifting objects which the submersible is incapable of handling alone. Systems used successfully in the past include lifting lines and buoyancy devices utilizing solid and liquid fuels or compressed gas. With the development of the Remote Unmanned Work System (RUWS), the capability exists to carry, locate, manipulate, and observe such auxiliary systems at depths of 20,000 feet.

The Deep Recovery System (DRS) program is an exploratory development effort of the Naval Sea Systems Command aimed at developing techniques and prototype hardware which will expand the recovery capability of deep ocean submersibles. One objective among several is to develop and demonstrate the technology for attaching and lifting objects weighing up to 200 pounds in water from ocean depths of 20,000 feet. Of the candidate systems for providing lift at 20,000 feet, the self-contained, buoyancy-type devices are preferred for use with cable-tethered submersibles. Although lift lines have been used successfully at shallow depths, the possibility of submersible entanglement increases with depth, particularly for RUWS, which uses a dual submersible-cable system. In addition, there exists the probable requirement that objects on the sea floor be moved from one location to another without being returned to the surface. This suggests that the lift device must be not only self-contained but also easily controlled.

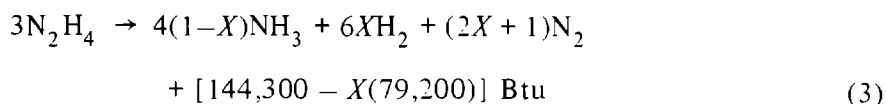
As described in Ref. 5, hydrazine decomposition is a promising gas source for deep ocean buoyancy applications. The objective of the work described in this report is to determine the decomposition efficiency of hydrazine decomposed on Shell 405 catalyst at actual ocean depths of 20,000 feet. This work was done under the auspices of the DRS program.

BACKGROUND

Hydrazine decomposition in the presence of a catalyst is a two step reaction:



where the second step absorbs a portion of the heat generated during the first step. The degree to which the second step goes to completion is a function of several variables, including temperature and pressure. The two equations above may be combined, resulting in



where X is the fraction of NH_3 dissociated in Eq. 2. The decomposition efficiency is said to increase as more and more ammonia is broken down into nitrogen and hydrogen. X then is a direct indicator of the reaction efficiency.

Although a considerable amount of hydrazine work has been done and several hydrazine decomposition systems operationally tested, at the beginning of this project, in July 1971, no data were available on the efficiency of hydrazine decomposition at pressures over 1000 psi. In April 1972, the Naval Weapons Center (NWC) completed the first phase of its hydrazine decomposition testing (Ref. 6). Extrapolating from the NWC test results obtained at 5000 psi, a buoyancy factor* of approximately 3.1 and an efficiency of $X = 0.54$ were predicted for hydrazine decomposition at 9000 psi. Although these values were not particularly encouraging and NWC cautioned against direct extrapolation, it was subsequently decided to go ahead with plans for deep ocean testing to obtain actual data for comparison with the laboratory data.

APPROACH AND OCEAN HARDWARE DEVELOPMENT

To determine the decomposition efficiency of hydrazine in the ocean, two systems, a gas generating system and an instrumentation system, were developed

* Buoyancy factor = weight of water displaced/weight of fuel used.

and integrated. The gas generating system, instrumentation electronics, and recorder were straightforward designs and changed very little during the program. Most problems occurred in integrating these two systems, particularly in designing the load cell sensor and in selecting the method of initiating hydrazine flow. Only the final system is described here. The gas generating system, sensors, and instrument package were integrated into a framework called the test unit (Fig. 1).

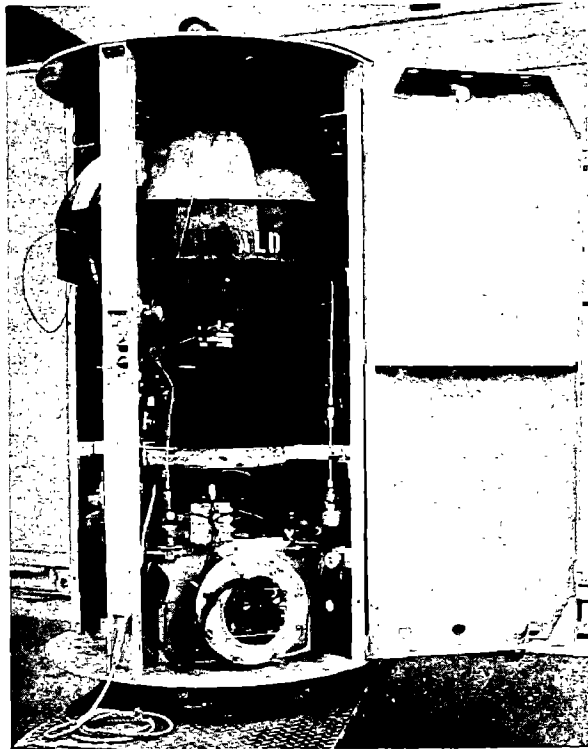


Figure 1. Test unit.

Gas Generation System

In the design of the gas generating system, the first consideration was the method of providing hydrazine to the reactor for decomposition. Several methods were available, including pumping, elastomeric expulsion, blowdown, and boot-strapping. Elastomeric expulsion was selected because it is simple and because it does not require any external power. Referred to as the hydrazine storage bladder, the elastomeric storage system receives hydrazine under pressure while expanding like a balloon. When filled, the bladder is shut off and ready to supply hydrazine to the reactor at a relatively constant pressure.

Once the hydrazine supply method was selected, the remainder of the system could be designed. The gas generating system whose performance was to be determined is shown schematically in Fig. 2. Converting this test bed system to a prototype operational unit is possible by condensing the structure and by replacing the solenoid valves with valves which can be operated by a submersible.

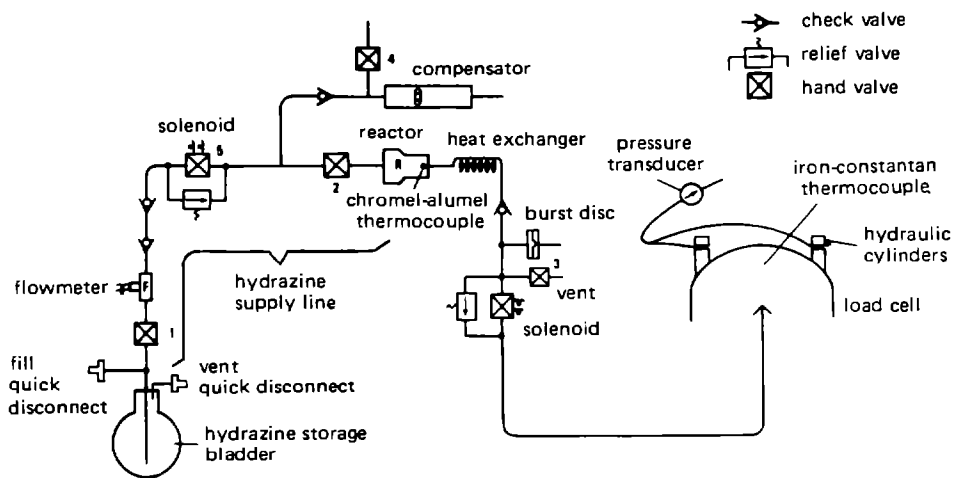


Figure 2. Schematic of gas generating system.

The hydrazine expulsion bladder was previously developed by Uniroyal, Inc., for the Civil Engineering Laboratory. It has a capacity of 7.2 gallons, or about 60 pounds of hydrazine. When received, the bladder expulsion pressure was fairly constant at 65 psig. When measured at the end of the program, the expulsion pressure had dropped to 45 psig. Its empty air weight is 36½ pounds.

The reactor (Fig. 3) is designed in accordance with the data contained in Ref. 7. Shell 405 spontaneous catalyst is used in a 2-inch-diameter by 5-inch-long bed. The reactor body is made of Inconel X-750 to decrease the possibility of annealing during testing. The cap screws are titanium and, except for the aluminum face seal for the cover plate, all other parts are stainless steel. The reactor will withstand a 3000-psi precharge, and is designed for a maximum flow rate of 0.0314 lb/sec, with a pressure drop of 10 psi maximum at ambient pressures greater than 100 psi. The injector plate has 19 holes, each 0.0156 inch in diameter, spaced to distribute the hydrazine as evenly as possible on the end of the catalyst bed.

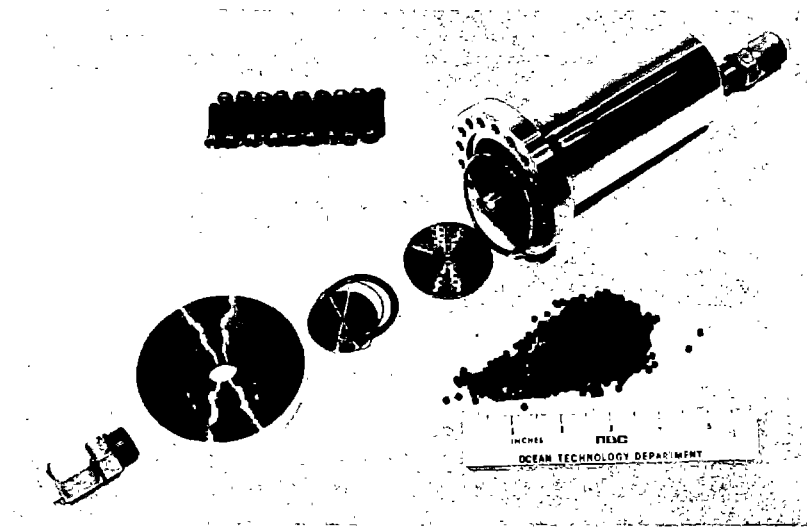
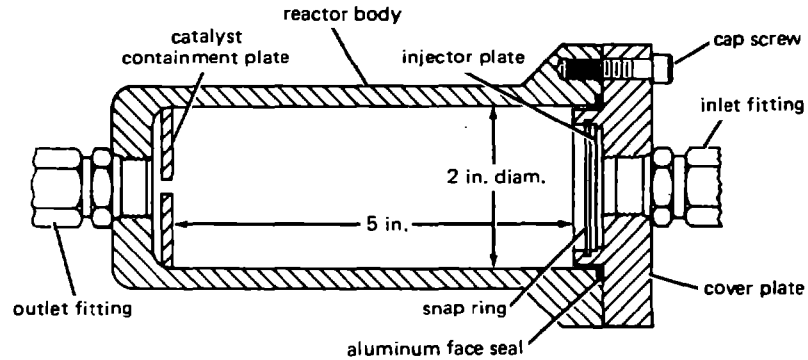


Figure 3. Reactor.

The compensator used in the test system is a 2-gallon, 3000-psi accumulator. It was used as the pressure compensator by charging it to one-sixth the expected operating depth pressure through valve 4 (see Fig. 2). The ratio of precharge pressure to operating depth pressure is determined easily from $p_1 V_1 = p_2 V_2$, given the system volume with the accumulator bladder expanded (V_1) and collapsed (V_2). As the system descends, the ambient pressure becomes equal to the system's internal pressure at one-sixth the operating depth. As the system continues down, the accumulator bladder collapses until the operating depth and complete collapse are reached simultaneously. This prevents a large pressure differential across the solenoid valves and a possible flooding of the catalyst bed when hydrazine flow is initiated.

The solenoid valves are special units purchased from Circle Seal Corp., James, Pond & Clark Division. The remainder of the gas generating system components and tubing are standard off-the-shelf hardware.

Instrumentation System

The design of the instrumentation system was based on a Century Electronics and Instruments Model 414 recording oscillograph. The oscillograph uses a tungsten filament lamp and Kodak Verichrome film and meets the requirements of MIL-0-23560/2 and BuWeps Drawing 1313040. The recorder galvanometers are driven by circuitry designed and built by the Quality Evaluation Laboratory, Naval Ammunition Depot, Oahu. The instrument package block diagram is given in Fig. 4. The actual package is shown in Fig. 5.

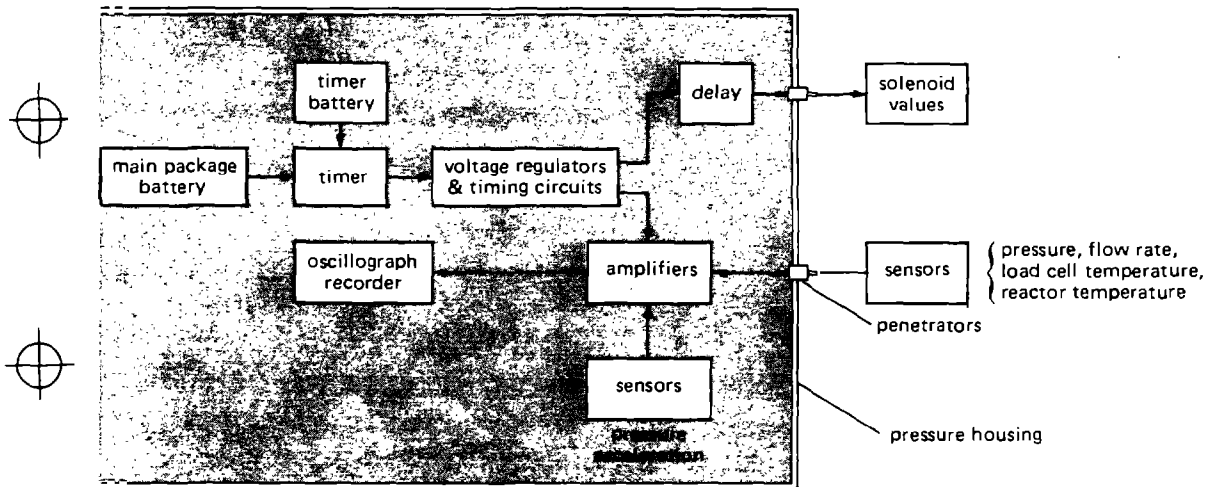


Figure 4. Instrumentation block diagram.

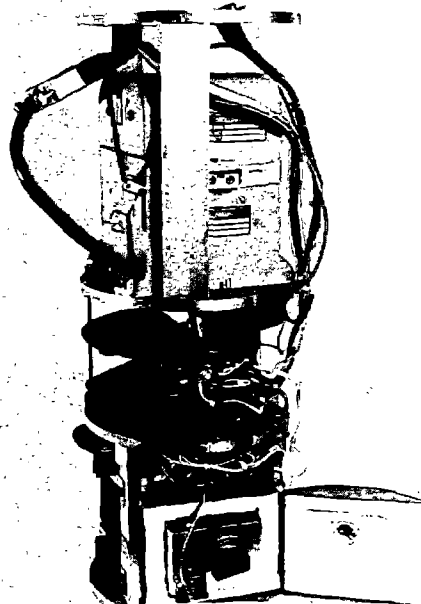


Figure 5. Instrument package.

The instrumentation package is contained in a pressure housing fabricated from a length of 4142 steel pipe with an outside diameter of 9¼ inches and a wall thickness of ¾ inch. End caps of 4140 steel completed the housing, which also acted as a ballast weight for the overall test unit. Connection is made through the end caps by single pin Marsh and Marine penetrators. The pressure housing and penetrators were hydrostatically tested at 9000 psi.

Although circuitry was provided to record 12 channels of data, only 6 were used. Sensors external to the pressure housing consisted of the following:

1. An iron-constantan thermocouple to measure the temperature of the gas in the load cell
2. A Chromel-alumel thermocouple to monitor the reactor temperature
3. An ITT-Barton Model 7509 turbine flow meter to measure the hydrazine flow rate
4. A load cell based on a Standard Controls Model 211-25-110, 0-100 psig, pressure transducer which measures the buoyancy of the generated gas

All sensors are standard units except the load cell. The load cell is the umbrella-like shell in the upper part of the test unit (Fig. 1). The gas is exhausted into this shell, which becomes buoyant and bears against hydraulic cylinders mounted to the frame as shown. The hydraulic pressure is measured by a pressure transducer which has been modified by drilling three holes in its case for pressure compensation.

All the electrical connections for these sensors were enclosed in oil-filled, pressure-compensated plastic housings and were connected to the pressure housing penetrators with Marsh and Marine submersible cable.

Inside the pressure housing were two more sensors: an accelerometer for measuring vertical accelerations and a pressure transducer which sensed the ambient ocean pressure through a passage in the end cap.

Two additional oscillograph channels were used for reference and timing traces.

The operation of the system and data reduction methods are described in Appendix A.

TEST PROGRAM

Although a substantial amount of testing was done, only the five tests performed with the finally configured test unit are described here.

Test at 1000 Feet

On 6 February 1974, a test was performed using the test unit to obtain data on the amount of lift provided per pound of decomposed hydrazine. The test was conducted in 1060 feet (486 psia) of water 4 miles offshore Kaneohe Bay from the largest NUC workboat, an LCM-8. Test time including transit was approximately 3½ hours and involved four persons. The test was performed in accordance with the NUC Hawaii Laboratory Test Procedure for Hydrazine Decomposition Tests, approved on 29 January 1974.

Data were reduced at three points along the oscillograph record; load cell data were reduced between two adjacent 80-second portions. The first 80-second data interval follows the first 5 seconds of reactor operation. This is usually a time of poor efficiency due to the relatively low reactor temperature. The second data interval includes data from 85 to 165 seconds and demonstrates significantly better reaction efficiency. Table 1 compares the 1000-foot test results with the performance predicted by NWC in Ref. 6.

Table 1. 1000-foot test results compared with NWC data.

Time (sec)	Lift per lb N_2H_4 (lb)	Ammonia Decomposition (X)	Reactor Temp (°F)	Bed Loading (lb/sec-in ²)
5-85	36.0	0.49	1030	0.0091
85-165	50.2	0.73	—	0.0079
NWC	52.7	0.79	—	—

Two basic problems were encountered during data reduction. The first problem, a drift in gain on the ambient pressure channel between the pretest and posttest calibrations, was easily resolved. The posttest calibration was used since it could be verified with the line counter reading. The second problem was not

so simple. Hydrazine flow rate oscillations of $\pm 50\%$ by weight at $3\frac{1}{4}$ Hz resulted in a data trace which was difficult to reduce. In this case, the trace was followed by planimeter to obtain an area which was then divided by the trace length. This appears to be a reasonable method of averaging, and the results so obtained are presented.

Since the NUC results were only some 5% below those obtained by NWC it was felt that the test unit was ready for deeper testing.

Test at 3000 Feet

A second test was run on 19 February 1974, in 2990 feet (1347 psia) of water 8 miles offshore Kaneohe Bay.

Data were reduced at nine points equally spaced along the oscillograph trace over a period of 4 minutes beginning 3 minutes after system initiation. Table 2 compares the test results with NWC predicted performance.

Table 2. 3000-foot test results compared with NWC data.

Time (sec)	Lift per lb N_2H_4 (lb)	Ammonia Decomposition (X)	Reactor Temp. (°F)	Bed Loading (lb/sec-in ²)
180-420	20.3	0.82	1287	0.009
NWC	17.7	0.70	—	0.002-0.015

Inspection of the data traces revealed a rather erratic but reducible load cell trace. A continuity check at the load cell pressure housing penetrators showed a resistance of less than 1000 ohms between the penetrator pin and the bottle. Flow meter oscillation amplitude was less than in the previous test, although several high-amplitude, low-frequency oscillations were observed toward the end of the run.

Since the data were suspect when compared with the previous test and with NWC predictions, it was decided to refurbish the pressure housing penetrators. It was also discovered that oil had been leaking from the load cell actuators due to the low ambient temperature. It was decided to repeat this test following repair and modification of the above items.

Test at 6000 Feet

In an effort to test in calm seas, the LCM-8 was taken to Pokai Bay, a small-boat harbor on leeward Oahu. It was planned to perform the 3000-foot and 6000-foot tests on the same day or on consecutive days. Reconsideration of the situation, however, resulted in performing the deeper test first. On 25 April 1974, a test was run at 6360 feet (2841 psia) some 8 miles offshore in mirror-smooth seas. The exceedingly flat sea surface turned out to be of special benefit. During retrieval of the test unit, a pushrod in the air motor which drives the line retrieval capstan jammed on its return spring and split a motor vane. The vane fragment caught in the small clearance of the motor rotor, and the pushrod end severely gouged the bore. This occurred with some 3500 feet of line out and the test unit negatively buoyant by about 200 pounds. The air motor was disassembled and repaired well enough to recover the test unit, a job which would have been difficult, if not impossible, in rough seas.

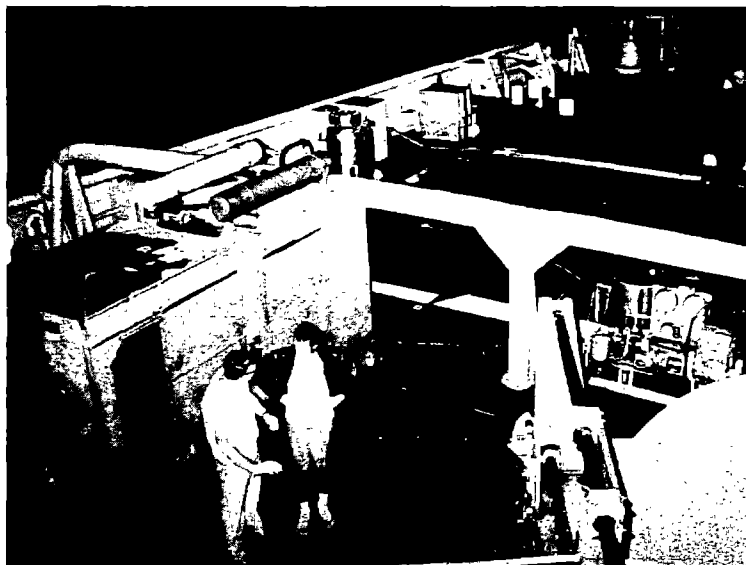
No decomposition data were obtained due to the partial crushing of the connector end of the load cell pressure transducer. The transducer had been inadequately pressure compensated. All other data channels were normal.

The transducer supplier was notified and another transducer was modified with larger compensating ports as a replacement before the deep ocean tests.

Deep Ocean Tests

On 18 June 1974, a test was performed in 15,000 feet of water 40 miles south of Oahu using the USS Beaufort (ATS-2) as an operational platform (Fig. 6). The test was conducted in accordance with the NUC Hawaii Laboratory

Figure 6. Test equipment aboard USS Beaufort for deep ocean tests.



Shipboard Test Specification, approved on 14 June 1974. The test procedure is essentially the same as used previously, the main difference being the line size and handling gear requirements.

When the test unit was returned to the deck following immersion, it was noted that the hydrazine bladder was still full. Inspection of the instrument package revealed that the system start-stop timer had ceased to run before starting the gas generator. Subsequent examination of the timer showed the failure to be due to a unique combination of timer attitude, low temperature, and marginal battery. A "fresh" dry cell had been installed prior to this test, but it had apparently degraded during its shelf time. The timer was then favorably oriented within the instrument package, insulated, and provided with a battery package consisting of four batteries wired in parallel.

Following these modifications the USS Beaufort was again utilized, and a test was performed at a depth of 17,700 feet northeast of Maui on 20 June.

After the test unit was retrieved, it was again noted that the hydrazine bladder was full. The entire test unit and instrument package were inspected and the following information assembled:

1. All the appropriate manual valves were open in the gas generating system.
2. A small amount of gas escaped the test unit near the surface, indicating that the compensator and downstream bypass relief valve had functioned properly.
3. During bleedoff of the remaining precharge pressure, a strong ammonia odor was noticed. This means that some hydrazine had passed either the upstream solenoid valve or the upstream relief valve, suggesting that (a) the solenoid valve opened or (b) the upstream manual throttling valve was open, pressurizing the volume between the solenoid valve and throttling valve to the ambient pressure, or both.
4. All wiring and connections were good, both internal and external to the instrument package.
5. The timer had been running continuously, as indicated by its position.
6. The oscillograph film had run completely through the recorder.
7. The data traces indicated the power surge to the solenoid valves (which are wired in series) and a constant depth of 17,700 feet (7879 psia) during the recorder run time.
8. The flow meter trace, although noisy, showed no hydrazine flow.

Additional pertinent information includes the following:

1. The solenoid valves were cycled in a pressure chamber at 9000 psi and 75°F prior to these tests.
2. The solenoid valve is a poppet-type design and should be insensitive to temperature.
3. The solenoid valves will open against upstream pressures in excess of 600 psi. With the upstream relief valve set at 250 psi, the opening of the solenoid is assured even under adverse pressure differentials.
4. Posttest system operation was normal.

DISCUSSION OF TEST RESULTS

Data obtained at 1000 feet correlate well with data gathered by NWC. The data taken at 3000 feet are suspect for three reasons:

1. They show an ammonia decomposition efficiency substantially better than that predicted by NWC.
2. The ammonia decomposition efficiency is markedly higher than that of the previous shallower test.
3. Partial shorting was observed by actual readings and electrical noise on the load cell channel.

The test unit failure at 17,700 feet was disappointing because no data were obtained and the cause of the failure was not readily apparent. To determine the cause of the system failure, it is necessary to consider two potential problem areas. The first, of course, is the possibility of equipment failure. However, all simple failure modes were examined without any specific mode becoming apparent. Further investigation in this area would necessarily include chamber testing at simulated depth and temperature. The second area to consider is the hydrazine itself. When hydrazine was initially considered for deep ocean use, it was noted that ocean bottom temperatures in the Atlantic are rarely lower than 35.6°F and in the Pacific not lower than 34.7°F. Since the freezing point of pure hydrazine is reported in the literature to be between 33.8°F and 35.6°F, it was felt that neat hydrazine could be used. Propellant-grade hydrazine (MIL-P-265366) is approximately 99% hydrazine and freezes at 33.6°F. Any further dilution will decrease the net lift available per pound of decomposed hydrazine.

An examination of properties such as freezing and boiling point, density, and viscosity indicates hydrazine to be very similar to water. A partial list of hydrazine and water properties is given in Table 3. The key to the behavior of

hydrazine under pressure in the ocean is given in the comparative densities of the liquid and solid phases. It is well known that the freezing point of water decreases with increasing pressure. However, it is not well known that this decrease is related thermodynamically to the fact that its density in the solid state is less than that in the liquid state. The relationship is described by a derivative of the Maxwell Equations (Ref. 4). Conversely, a substance whose solid density is greater than its liquid density will have a freezing point which increases with increasing pressure (Fig. 7 and 8).

Table 3. Properties of hydrazine and water.

Property	N_2H_4	H_2O
Freezing, $^{\circ}C$	1-2	0
Density Solid	1.146 ($-5^{\circ}C$)	0.90
Liquid	1.025 ($0^{\circ}C$)	0.9999
	1.0085 ($20^{\circ}C$)	0.9982
	0.9801 ($50^{\circ}C$)	0.9881
Boiling Point (760mm), $^{\circ}C$	113.5	100
Viscosity ($5^{\circ}C$), centipoise	1.21	1.5188
Heat of formation, cal/mole	12,000	-68,317
Heat of combustion, cal/mole	-148,600	--
Heat of fusion, cal/mole	3025	1436
Heat of vaporization, cal/mole	10,700	9729
Entropy of liquid ($25^{\circ}C$), cal/mole- $^{\circ}$	29.01	28.1
Entropy of solid ($2^{\circ}C$), cal/mole- $^{\circ}$	16.14	--

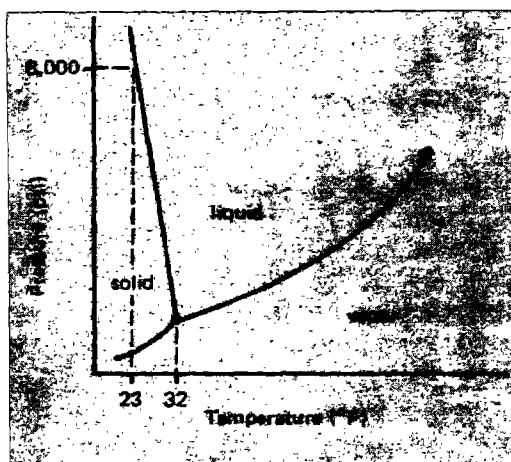


Figure 7. Phase diagram for water.

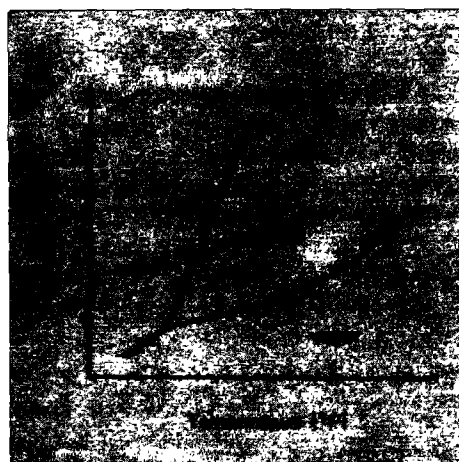


Figure 8. Phase diagram for a substance which contracts on freezing.

When the heat transfer situation is examined analytically, it can be shown that the hydrazine should indeed freeze in the 0.25-inch-diameter stainless steel hydrazine supply line (see Fig. 2). This analytical prediction is based on several assumptions which, of course, are open to discussion. These assumptions are:

1. The unit surface conductance for the external tube surface is 10 Btu/hr-ft²-°F.
2. The thermal conductivity of frozen hydrazine is approximately that of ice, 1.34 Btu/hr-ft²-°F.
3. The temperature at which hydrazine will freeze has been reached by 6000 feet during descent—that is, the time interval for freezing of the hydrazine begins when the test unit reaches 6000 feet during descent.

Based on these assumptions and others as described in Ref. 4, the time required for the liquid-solid phase change in the hydrazine line can be determined if an ocean temperature of 34.8°F is assumed:

<u>N₂H₄ Freezing Temp (°F)</u>	<u>Time to Freeze Solid (min)</u>
35.6	204
38.0	51
40.0	32
43.6	19

The test unit was below 6000 feet for 90 minutes and at 17,700 feet for over half an hour.

Since hydrazine is a polar liquid like water, it seems reasonable to assume that it has a similar solid-liquid phase line on its pressure-temperature diagram but with opposite slope. Specifically, at 8000 psi, the freezing point of water has dropped 8.5°F to 23.5°F. Inferring an equivalent but opposite slope on the hydrazine phase line gives a freezing point of between 42.3°F and 44.1°F, well above 34.8°F, the ocean temperature.

To further aggravate the situation, the hydrazine inlet line includes a stainless steel mesh, 10-micron filter. This filter is a prime site for freezing, even if the freezing temperature of hydrazine were increased only a few degrees.

With these considerations in mind, it was apparent that a relatively simple laboratory experiment could verify the possibility of frozen hydrazine preventing system operation.

LABORATORY TESTS

Test Apparatus

It was decided to measure the freezing point of hydrazine by the method described in ASTM D1177-65, Standard Method of Test for Freezing Point of Aqueous Engine Antifreeze Solution. A pressure bomb was fabricated from 1½-inch-diameter stainless steel bar. The bar was 6 inches long with a 3/8-inch-diameter bore. The ends were threaded to accept a thermistor and pressurizing fitting. A piston was fabricated to separate the hydrazine and pressurizing oil. The bomb was pressurized with a dead-weight gage-tester hand pump, and a cold bath was provided by an ice and alcohol mixture. The test apparatus and thermistor schematic are shown in Fig. 9.

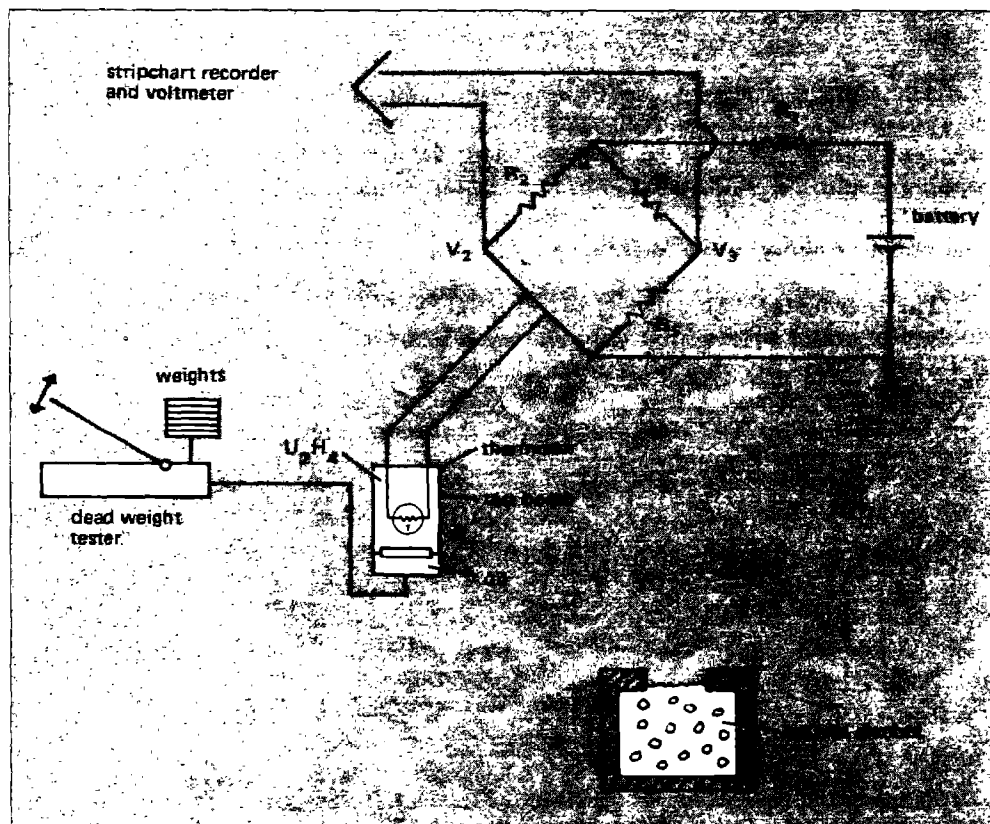


Figure 9. Test apparatus and schematic.

The hydrazine temperature was measured with a thermistor inserted in the hydrazine end of the bomb. A thermistor is a temperature-sensing unit whose resistance changes with temperature. The resistance of the thermistor was determined with an unbalanced Wheatstone bridge. Voltage across the bridge was measured with a digital voltmeter and recorded on a strip chart recorder. Since the input impedance of the voltmeter and recorder were on the order of hundreds of megohms while the bridge resistances were about 20,000 ohms, the thermistor resistance, R_t , can be found from:

$$R_t = \frac{R_5 R_2 V_1 + R_2 (R_3 + R_5) (V_2 - V_3)}{R_3 V_1 - (R_3 + R_5) (V_2 - V_3)} \quad (4)$$

Voltage to the bridge was provided by a dry cell and was constant to within a few percent throughout the tests. It was measured, however, before each test.

The voltage-dropping resistor, R_1 , was changed during the course of the experiment. It was originally 400,000 ohms, which resulted in a full-scale temperature range of 16°F on the strip chart recorder and a corresponding resolution limit of 0.08°F. R_1 was later changed to 870,000 ohms for a full-scale range of 33°F and a resolution limit of 0.16°F.

The thermistor was calibrated from 30°F to 60°F by immersion in an ice-alcohol-water bath whose temperature was measured with a 24-inch 30°F-100°F mercury thermometer with a resolution limit of 0.1°F. The thermistor was calibrated with the same bridge, digital voltmeter, and strip chart recorder setup used during the tests. This eliminated such second-order effects as the finite impedance of the voltmeter and recorder.

Tests were performed by pressurizing the bomb and placing it in a cold bath. After the hydrazine had frozen, the bomb was removed from the bath and warmed in air to obtain the thawing temperature. Finally the pressure was released. The recorder was run continuously in all tests but test 2, and several data points were taken from the voltmeter during each run.

To reduce the data, the strip chart was calibrated for millivolts versus chart displacement. The resulting millivolt reading is the bridge imbalance which can be converted to thermistor resistance. The temperature can then be obtained from the thermistor calibration curve.

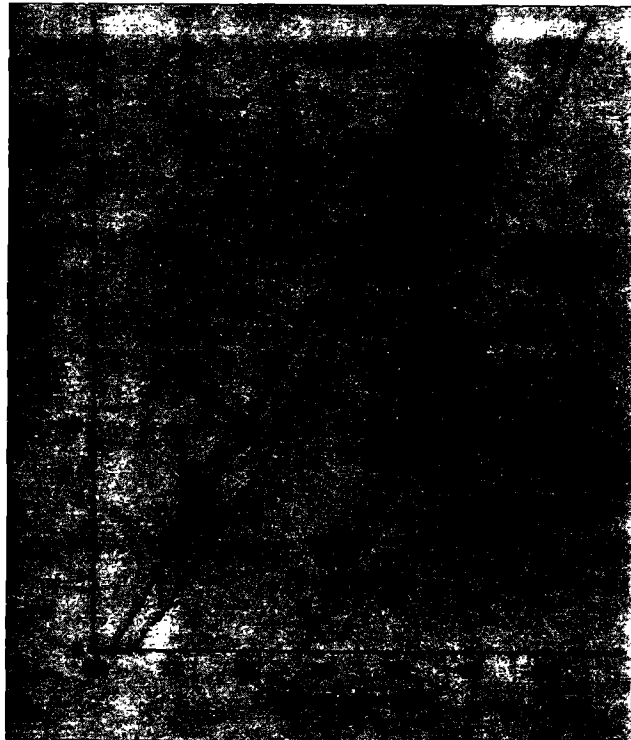
Test Results

The test results are listed in Table 4 and plotted in Fig. 10.

Table 4. Test results.

Test	Pressure (psia)	Supercool Temp (°F)	Freezing Temp (°F)	Thawing Temp (°F)	Uncertainty (°F)
1	8000	35.5	39.0	39.9	± .26
2	8000	—	39.4	39.7	± .25
3	8000	—	39.4	40.0	± .25
4	6000	26	37.4	38.4	± .25
5	6000	25	37.6	38.6	± .25
6	3000	did not freeze: limit of cooling approx 18°F			
7	3000	did not freeze: limit of cooling approx 22°F			
8	3000	17	34.2	35.2	± .33
9	3000	16.5	33.9	35.2	± .33
10	14.7	10	30.4	30.9	± .33
11	14.7	12	30.4	30.6	± .33
12	14.7	24	30.5	31.2	± .25
13	3000	no supercool	33.8	34.4	± 1.5
14	3000		33.8	35.0	± 1.5
15	6000	30.3	37.3	37.9	± 1.5
16	8000	24.5	39.6	40.6	± 1.5

Figure 10. Freezing temperature
versus pressure.



Discussion

The freezing point-pressure profile as determined by this experiment is displaced to the left (colder) of the theoretical curve for pure hydrazine, as shown in Fig. 10. This displacement is due to water dissolved in the hydrazine. From the freezing point at 14.7 psia, the amount of water is estimated at 2.5%, a reasonable amount for propellant-grade hydrazine. The theoretical curve was derived from the Clapeyron equation as described in Appendix B.

The significance of the depressed freezing point is apparent in Fig. 11, where the approximate ocean temperature is plotted as a function of depth (pressure). The ocean temperature is less than the experimentally determined freezing temperature of hydrazine at depths below about 9500 feet.

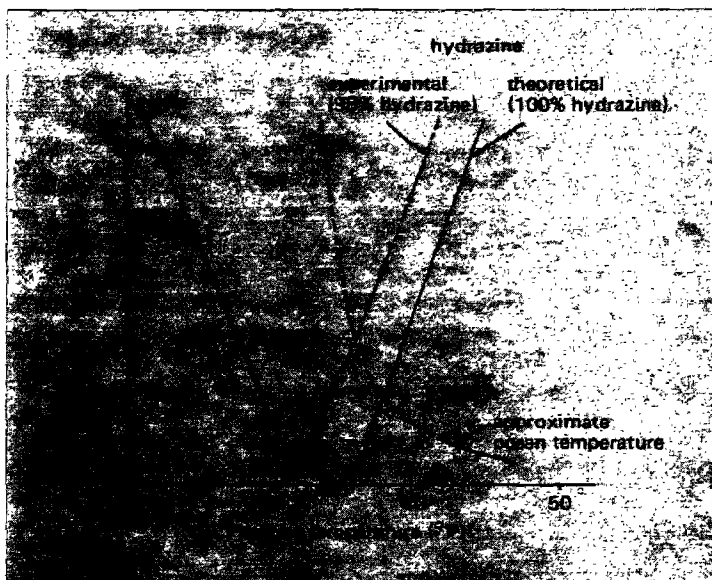


Figure 11. Comparison of the liquid-solid phase diagram for water and 98% hydrazine.

It is also noted from Fig. 10 that the experimental profile is not parallel to the theoretical profile but becomes closer at the higher pressures. It is suspected that as the freezing point of the mixture components diverges with pressure the hydrazine tends to crystallize out, giving the appearance of a more pure substance than actually exists. This effect may be due to the bath temperature and cooling rate.

The hydrazine exhibited supercooling in all but one of the tests. This was due to the inaccessibility of the hydrazine for stirring and seeding as described in the ASTM test standard. The state of the liquid hydrazine when in the supercooled state is very fragile, as demonstrated during test 4. In this test the bomb was tapped with a wrench just as the trace went off the chart scale. The vibration was sufficient to induce crystallization, as indicated by the immediate peaking of the trace to the recorded freezing temperature. This is significant since system handling or the shock of a valve opening may cause rapid freezing when the hydrazine has been supercooled.

A final observation was made while emptying the bomb. The hydrazine, normally a clear, water-like liquid, had become milky. Although a small amount of oil was found in the hydrazine (oil is insoluble in hydrazine), the milky appearance is apparently due to having pressurized the hydrazine at low temperatures. The same observation was made during the shipboard tests and also while emptying another system which had spent several months at 6000 feet. The relationship of this appearance to the physical properties of hydrazine is unknown.

CONCLUSION

1. Neat or propellant-grade hydrazine cannot be used at ocean depths below approximately 9500 feet without a means of preventing freezing.

RECOMMENDATIONS

1. A more sophisticated apparatus should be assembled to determine the freezing point of candidate hydrazine mixtures. Although the author feels that the equipment used in the freezing experiment was adequate to demonstrate the general situation, the presence of oil in the hydrazine may have had some effect, and consequently the data are not adequate for system design purposes.
2. To determine the most efficient fuel, laboratory apparatus should be used to decompose, under pressure, the prime hydrazine mixture candidates. Temperature control to simulate deep ocean temperatures is highly desirable.
3. The hydrazine test unit or a similar apparatus should then be used to test the most efficient fuel.

blank

Appendix A

SYSTEM OPERATION AND DATA REDUCTION

SYSTEM OPERATION

The test unit operation is described briefly as follows:

1. Calibrate the instrument package and charge and install the battery.
2. Fill the storage bladder with hydrazine.
3. Charge the compensator to at least one-sixth the anticipated operating depth.
4. Set the instrument package timer and install the package in the pressure housing.
5. Lower the test unit to its operating depth; wait for sufficient time to elapse and retrieve the unit.
6. Disarm the unit.
7. Develop the oscillograph film and reduce the data to obtain flow and lift rates, temperature, and ambient pressure.

DATA REDUCTION

The data reduction method is typical of that used with oscillograph recording systems. After the trace deflections are calibrated with known inputs before and after each test, the deflections obtained during the tests can be correlated with specific sensor input values. These values were recorded over a 15-minute interval beginning 5 seconds before the initiation of hydrazine flow. The time history is required, except for the load cell, to obtain average sensor readings over specific time intervals. The data taken from the load cell trace is the change in pressure (load) over the specified time interval. The data taken from the traces are therefore of the form shown in Table A-1, where all data but those for the load cell are averaged over the time period $(T_n - T_{n-1}) = \Delta T_{n-1}$.

Table A-1. Data format.

Time (sec)	Av. Load Cell Temp. (°F)	Av. Flow Rate (lb/sec)	Av. Ambient Pressure (psia)	Load Cell (lb)
T_{n-1}				F_{n-1}
ΔT_{n-1}	T_{n-1}	Q_{n-1}	P_{n-1}	
T_n				F_n
ΔT_n	T_n	Q_n	P_n	
T_{n+1}				F_{n+1}

From these data the buoyancy or gas generation rate, L , may be found from

$$L_{n-1} = \frac{F_n - F_{n-1}}{T_n - T_{n-1}} \quad \text{lb/sec} \quad (\text{A-1})$$

When L is divided by the average flow rate, the amount of net buoyancy per pound of hydrazine is obtained directly:

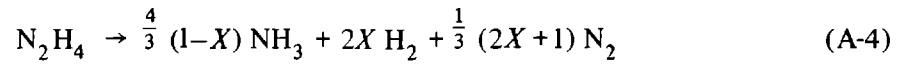
$$B_n = L_n / Q_n \quad \text{lb net lift/lb N}_2\text{H}_4 \quad (\text{A-2})$$

Furthermore, the ammonia decomposition efficiency may be calculated from the above data using the relationships

$$pV = ZmRT \quad (\text{A-3})$$

where p = pressure
 V = volume
 Z = compressibility factor
 m = mass
 R = gas constant
 T = temperature

and



where X = ammonia dissociation

to derive

$$X = \frac{4.478 \frac{Bp}{\rho T} - 0.5 Z_{\text{N}_2}}{Z_{\text{N}_2} + 3 Z_{\text{H}_2}} \quad (\text{A-5})$$

where B = net buoyancy per lb N_2H_4 (lb)
 p = ambient pressure (psia)
 ρ = ambient water density (lb/ft³)
 T = ambient temperature (°R)
 Z_{N_2} = nitrogen compressibility factor
 Z_{H_2} = hydrogen compressibility factor

Appendix B

THEORETICAL FUSION LINE FOR HYDRAZINE

The Clapeyron equation, a derivative of the Maxwell equations, relates the slope of the saturation pressure-temperature line, the latent heat, and the change in volume during a change in phase. The equation is:

$$\frac{dp}{dT} = \frac{h'' - h'}{T(\nu'' - \nu')} \quad (\text{B-1})$$

where $h'' - h'$ = the heat of fusion (for freezing), Btu/lb
 ν'' = the specific volume of the liquid, ft³/lb
 ν' = the specific volume of the solid, ft³/lb
 p = pressure, psia
 T = temperature, °R

$$\text{if } k = \frac{h'' - h'}{\nu'' - \nu'}$$

$$\text{then } dp = \frac{k}{T} dT$$

To find the freezing temperature at any pressure knowing the freezing temperatures T_{fa} at atmospheric pressure, integrate between 14.7 and p and T_{fa} and T :

$$\int_{14.7}^p dp = k \int_{T_{fa}}^T \frac{dT}{T}$$

$$\frac{p - 14.7}{k} = \ln T - \ln T_{fa}$$

or

$$T = T_{fa} e^{\left(\frac{p - 14.7}{k}\right)} \quad (\text{B-2})$$

Using the values in Table 3 including ν' at -5°C , since no value has been obtained at 0°C :

$$k = 5.56 \times 10^5 \text{ lb/in}^2$$

$$\text{and } T = T_{fa} e^{\left(\frac{p - 14.7}{5.56 \times 10^5}\right)} \quad (\text{B-3})$$

This relationship is easily calculated for the freezing temperature (T_{fa}) range limits of 33.8° to 35.6°F (Table B-1). The values derived from the upper limit were used in Fig. 10 and 11.

Table B-1. Freezing temperature versus pressure.

Pressure (psi)	Freezing Temperature Range ($^{\circ}\text{F}$)	
0	33.8	35.6
1000	34.7	36.5
2000	35.6	37.4
3000	36.5	38.3
4000	37.3	39.2
5000	38.2	40.1
6000	39.1	41.0
7000	40.0	41.9
8000	40.9	42.8
9000	41.8	43.7
10000	42.7	44.6

BIBLIOGRAPHY

1. American Society of Metals. Metals handbook, Vol. 1, 8th ed. Metals Park, Ohio.
2. Dietrich, G. General oceanography. Wiley and Sons, New York, 1957.
3. Jones, J. B., and Hawkins, G. A. Engineering thermodynamics. Wiley and Sons, New York, 1960.
4. Kreith, F. Principles of heat transfer. International Textbook Co., Scranton, Pa., 1958.
5. Naval Weapons Center. A study of gas generators for ship salvage systems, by J. T. Bryant, China Lake, Calif. Aug. 1970. NWC TP 4953.
6. _____. Decomposition of hydrazine on Shell 405 catalyst at high pressure, Part 1, 500-5000 psi, by S. E. Wood and J. T. Bryant. China Lake, Calif. Dec. 1972. NWC TP 5367.
7. Rocket Research Corp. Development of design and scaling criteria for monopropellant hydrazine reactors employing Shell 405 spontaneous catalyst. Seattle, Washington, 19 Jan. 1967. (RRC-66-R076, Vol. I, II) (Work performed under NASA Contract NAS 7-372.)
8. _____. Monopropellant hydrazine design data handbook. York Center, Redmond, Wash.
9. Westinghouse Electric Corp. Final report for a technical analysis and design of an emergency deballasting and/or variable ballast control system. N00024-69-C-5480.